

(18)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 328 047  
A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 89102096.8

(22) Date of filing: 08.02.89

(61) Int. Cl.<sup>4</sup>: **C09D 5/24 , C08L 81/06 ,  
C08K 3/04 , C08K 3/08 ,  
H01B 1/20 , //H01G4/00**

(30) Priority: 12.02.88 US 155188

(43) Date of publication of application:  
16.08.89 Bulletin 89/33

(84) Designated Contracting States:  
**AT BE CH DE ES FR GB GR IT LI LU NL SE**

(71) Applicant: **EMERSON & CUMING, INC.**  
25 Hartwell Avenue  
Lexington, MA 02173(US)

(72) Inventor: **Sullivan, Mary**  
41 Teller Street  
Marlboro Massachusetts 01752(US)

(74) Representative: **UEXKÜLL & STOLBERG**  
Patentanwälte  
Beselerstrasse 4  
D-2000 Hamburg 52(DE)

(54) **Solvent-processible electrically conductive coatings.**

(57) Novel solvent processible electrically conductive coatings of conductive particle (e.g. silver) filled polysulfones. The coating compositions are useful in a variety of environments, especially in the manufacture of tantalum capacitors. The coatings advantageously are extremely heat stable to withstand high temperature soldering and attach to solder without thermal decomposition.

**EP 0 328 047 A1**

## SOLVENT-PROCESSIBLE ELECTRICALLY CONDUCTIVE COATINGS

### Background of the Invention

The present invention relates to solvent-processible conductive coatings, and more particularly to  
 5 electrically conductive coatings of electrically conductive particle filled polysulfones.

Electrically conductive coatings are widely used in the electronics, defense and aerospace industries in conjunction with metals and plastics for electrostatic discharge electroless plating applications, in EMI/RFI shielding and in solder attach applications. Solvent processible polymer systems currently employed in this field include thermoplastic acrylics and polyesters, and thermosetting epoxies and acrylics, all of which  
 10 have well known limitations. The thermoplastic systems, when filled with electrically conductive particles, exhibit excellent conductivity and are readily processible at low cure temperatures and short cure times. Unfortunately, these systems often exhibit limited chemical and temperature resistance properties which restrict their use.

Electrically conductive coatings used in capacitor construction, as well as in some of the previously  
 15 mentioned applications, must be capable of forming a sturdy bond to solder (i.e., they must be "solderable") with good electrical contact. Solderability occurs through conductive particle-to-solder contact. The standard thermoplastic solderable coatings are acrylic or polyester based and decompose or degrade when heated to the 185 to 250 °C temperatures of soldering. While this decomposition is necessary to allow the solder to attach directly to the conductive particle filler, the decomposition or degradation is unpredict-  
 20 able and can undesirably spread beyond the solder attach site. Such undesired decomposition or degradation usually diminishes the electrical properties of the coating and the function of the entire article.

The thermosetting epoxies and acrylics, when filled with conductive particles, show improved chemical and temperature resistance in many applications. Such compositions often require prohibitive time/temperature cure profiles, have limited useful life and do not exhibit appreciable solderability.

25 The present invention finds particular utility as one of the conductive layers of tantalum capacitors. The layers surrounding the tantalum core of such capacitors most frequently are created by dipping the core in a series of baths containing a material to be deposited in an appropriate solvent. Thus, this "solvent processibility" is quite important in this field of use for conductive coatings.

Accordingly, it is an object of the invention to provide solvent processible electrically conductive  
 30 coatings.

Another object of the invention is to provide such conductive coatings which exhibit good adhesion to a variety of substrates, form a sturdy bond to solder and are stable when exposed to high temperatures, i.e., those encountered during soldering.

A further object of the invention is to provide such conductive coatings which exhibit excellent electrical  
 35 properties.

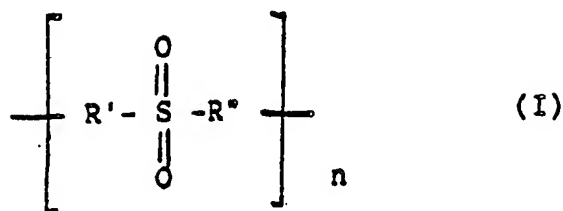
### Summary of the Invention

40 The foregoing and other objects of the invention are attained by the present solvent processible electrically conductive particle filled polysulfone compositions.

Polysulfone materials are widely available. Their primary use has been as a solid plastic for injection-molded parts. Polysulfones have been combined with a variety of fillers, including glass and metal fillers in  
 45 order to provide structural reinforcement and shielding effectiveness.

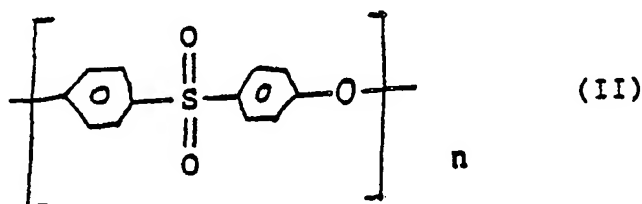
Polysulfones, being classified as "engineering thermoplastics", advantageously exhibit high thermal stability, excellent chemical resistance to aqueous mineral acids, alkali, salt solutions, oils and greases. While these properties make polysulfone-molded parts quite attractive for various uses, they also have lead to relatively little interest in their use in solvent processing applications.

50 As used herein, "polysulfone" means any polymer having repeating groups containing sulfone (O=S=O) groups i.e., polymers containing repeating groups of the general formula (I):



Any particular identities of R', R'' and n are not required. A wide variety of polysulfones are available. For example, R' and R'' independently can contain one or more groups selected from aryl, alkyl, alkaryl, aralkyl, phenoxy and sulfone among others. R' and R'' independantly can include internal ether linkages. Virtually all commercially useful polysulfones are of the above formula wherein both R' and R'' contain aryl groups; these are the aromatic thermoplastic resins known for superior properties. Preferred polysulfones include ether linkages between repeating groups. The number of repeating units (n) varies among the various commercially available polymers. In general, useful polymers are of 10,000 to 50,000 (no. average) molecular weight.

The most preferred polysulfone is Victrex polyether sulfone (trademark of ICI) which is of the formula (II):



wherein n = about 95 and the molecular weight (no. average) is about 22,000. When those skilled in the art refer to "polyether sulfone", the above polymer of formula II often is intended. Other polysulfones exhibiting excellent physical properties, and included within the scope of the present invention, include Udel polysulfone (Union Carbide Corp), Astrel 360 polyarylsulfone (Carborundum Company), and Radel polyphenylsulfone (Union Carbide Corp.) all of which are referenced in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 18, page 833, as "four basic sulfone polymers".

The Polysulfones are solids and thus must be placed into solution for further processing according to certain preferred embodiments of this invention. While the use of any particular solvent (or combination of solvents) is not required, the solvent should be compatible with the polysulfone such that the polysulfone dissolves and remains dissolved therein. Examples of useful solvents include N-methyl pyrrolidone, N-ethyl pyrrolidone, N-hydroxyethyl pyrrolidone, dimethyl formamide and butyrolactone.

As the polysulfones themselves are non-conducting, they must be filled with conductive particles. A "particle" as this term is used herein does not limit the geometry of the filler material and includes spherical, plate-like, fibrous and irregularly shaped particles and combinations thereof. The invention is not limited to the use of any specific conductive particle. Examples of conductive particles include those of silver, gold, platinum, copper, nickel, tin and other conductive elemental metals, and alloys or other combinations thereof, those of carbon, and those of non-conducting material having a conducting material coated thereon or filled therein such as silver-plated glass particles and nickel-plated mica particles. Average particle size of conductive particles typically ranges from a fraction of a micron to hundreds of microns in diameter; silver particles from 1 to 20 micron diameter, especially 5 to 8 microns, are especially preferred. The choice of the size, shape and content of the particles often depends on the final use for the conductive coating and is with the artisan's skill.

The composition of the present invention which are capable of being coated onto a substrate include polysulfone resin, electrically conductive particles and suitable solvent. After application to a substrate, the solvent is driven off (preferably aided by the application of heat) to leave behind a solid coating of electrically conductive particle filled polysulfone. The lower and upper limits of the amount of electrically conductive filler in the composition is functionally defined: the lower limit being that which is sufficient to give the desired electrical conductivity and the upper limit being the critical pigment volume concentration above which the coating fails to maintain useful structural integrity. These lower and upper limits depend on the make-up of the conductive particles as well as their size and shape. Particular limits are readily determined by the artisan. In general, a solid coating containing at least about 50% by weight of electrically

conductive particles, based on the total weight of the coating, is preferred. More preferred are coatings containing about 66 to 95% by weight of filler.

The compositions capable of forming a solid coating, i.e. the solvent-containing compositions, are prepared by first dissolving polysulfone resin in solvent. A solution containing about 15 to 25 weight % resin is preferred. Conductive particles are mixed into the polysulfone solution in an amount sufficient to provide the desired electrical properties, without exceeding the critical pigment volume concentration, in the solid coating. In general, 20 to 60 wt. %, preferably 30 to 50 wt. %, based on the weight of the solution is used. The desired final viscosity is obtained by adding additional solvent, preferably along with another volatile organic liquid such as toluene or xylene. For compositions used to dip-coat substrates, a final viscosity of 250 to 500 cps at 25° is preferred.

Silver filled polysulfone compositions according to preferred embodiments are prepared by dissolving 15 to 25 wt. % Victrex 4800 G PES (I.C.I.) in 85 to 75 wt. % N-methyl pyrrolidone. As the PES is not easily dissolved, mixing is employed until a lump free consistent solution is obtained. Silver flake is mixed into the resulting PES solution at the preferred concentration of 30 to 50% by weight, based on the weight of the total. Mixing sufficient to thoroughly wet the silver is desired. Additional N-methyl pyrrolidone as well as toluene is added at this stage to provide the desired final viscosity.

The following example illustrates a specific embodiment of the present invention:

#### EXAMPLE ONE

A silver filled polyether sulfone solution is prepared by dissolving 25 pph (parts per hundred weight) polyether sulfone (Victrex 4800G, ICI) of formula (II) in 75 pph N-methyl pyrrolidone. As the polyether sulfone is not easily dissolved, the container is rolled for 48 to 72 hours until a lump free consistent solution results. 37.5 pph of the resulting PES solution, 5.4 pph N-methyl pyrrolidone and 10.8 pph toluene are combined in the bucket of a Ross double planetary mixer and mixed thoroughly. 30 pph Metz No. 9 silverflake (nominal 5 micron diameter) is gradually added to the mixture while stirring gently until the silver is thoroughly wet out. The mixture is degassed under vacuum and the viscosity is adjusted to the desired 300 to 350 cps (25° C, Brookfield No. 2, 100 rpm), by the addition of 6.3 pph N-methyl pyrrolidone, and 10 pph toluene.

The resulting solution is used in the preparation of a solderable silver-containing layer of tantalum capacitors via a dip-coating process. The coating imparts to the capacitors excellent capacitance, low dissipation factor (DF) and low equivalent series resistance (ESR). Importantly, the values of these properties fall within a narrow range and are readily reproducible. While conventional acrylic coatings often result in capacitors which become less efficient (increased DF and/or ESR) after packaging (soldering), the use of the present inventive coatings provides capacitors which can exhibit increased efficiency after packaging and improved long-term high temperature stability.

In the following table capacitance (CAP) in picofarads and % DF, both measured at 1 kHz, is compared among tantalum capacitors employing conventional acrylic-based silver-filled coatings, thermoplastic epoxy-based silver-filled coatings and Victrex PES-based silver-filled coatings. The use of a thermoset epoxy-based coating failed as it was not solderable. Dilution, viscosity, silver-to-resin ratio and type of silver particles was constant to enable direct comparisons. The reported values were taken after silver coating and again after soldering.

Coating	Coated		Soldered	
	CAP	%DF	CAP	%DF
Acrylic	237	7.7	233	8.48
Epoxy	236	8.31	228	8.7
PES	232	8.09	223	6.7

As seen in the data above, tantalum capacitors containing silver-filled coatings of the present invention exhibited marked improvement in both capacitance and DF when compared to known materials.

Although the invention has just been described in connection with a preferred embodiment, it is not so limited. Modifications within the spirit and scope of the claims will be apparent to those skilled in the art.

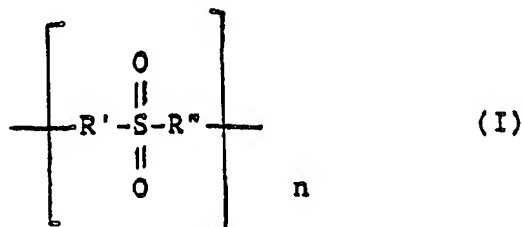
## Claims

1. A coated article comprising a substrate and an electrically conductive coating thereon, the coating comprising conductive particle filled polysulfone.

2. An article of claim 1 wherein said conductive particles comprise silver.

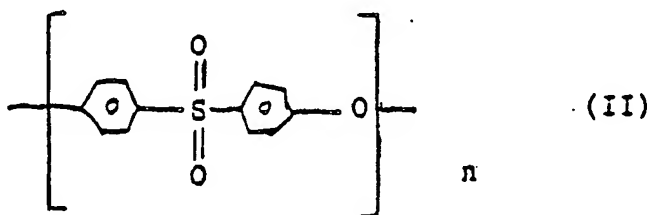
3. An article of claim 1 wherein said conductive particles are selected from the group consisting of conductive elemental metal, carbon, and nonconducting particles having a conductive material coated thereon or filled therein.

4. An article according to any of claims 1 to 3 wherein said polysulfone is of formula



wherein R' and R'' independently include one or more groups selected from alkyl, aryl, aralkyl, alkaryl, alkoxy, phenoxy and sulfonyl and wherein n is such that the number average molecular weight is about 10,000 to 50,000.

5. An article according to any of claims 1 to 3 wherein said polyether sulfone is of formula



wherein n is about 95.

6. An article of claim 1 wherein said substrate comprises tantalum.

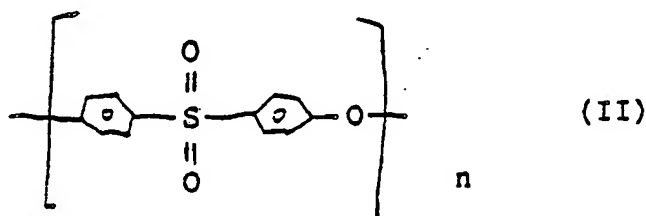
7. An electrically conductive coating composition comprising electrically conductive particles and polysulfone.

8. A composition of claim 7 wherein said conductive particles comprise and electrically conductive metal.

9. A composition of claim 7 wherein said conductive particles comprise silver.

10. A composition of claim 7 wherein said conductive particles comprise carbon.

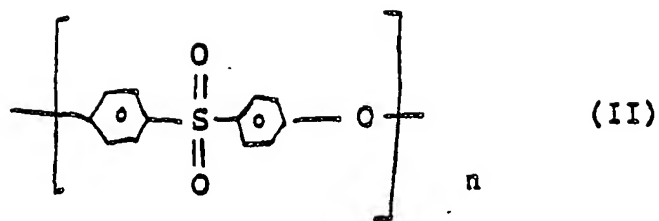
11. A composition according to any of claims 7 to 10 wherein said polyether sulfone is of formula



wherein n is about 95.

12. A composition capable of being coated onto a substrate and comprising electrically conductive particles, polysulfone and solvent for polysulfone.

13. A composition of claim 12 wherein said polyether sulfone is of formula



10 wherein n is about 95.

14. A composition of claim 12 wherein said conductive particles comprise electrically conductive metal.

15. A composition of claim 12 wherein said conductive particles comprise silver.

16. A composition of claim 15 wherein said solvent comprises pyrrolidone.

17. A composition of claim 16 wherein said solvent comprises N-methyl pyrrolidone.

15 18. An electrical capacitor comprising an electrically conductive layer of electrically conductive particle filled polysulfone.

20

25

30

35

40

45

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 596 670 (N. LIU) * Claims 1-2; column 5, line 52 - column 6, line 48; column 13, lines 33-52 * ----	1,12	C 09 D 5/24 C 08 L 81/06 C 08 K 3/04 C 08 K 3/08 H 01 B 1/20 // H 01 G 4/00
X	GB-A-1 234 954 (ATELIERS DE CONSTRUCTION ELECTRIQUES DE CHARLEROI) * Claim 6; example 3 * ----	1,3-5,7 ,8,10- 13	
X	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 192 (C-429)[2639], 19th June 1987; & JP-A-62 15 231 (MITSUBISHI RAYON CO., LTD) 23-01-1987 * Abstract * -----	1-17	
			TECHNICAL FIELDS SEARCHED* (Int. Cl.4)
			C 08 K C 08 L C 09 D H 01 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18-05-1989	Examiner HOFFMANN K.W.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

(19)



Europäisches Patentamt  
Best Available Copy  
European Patent Office  
Office européen des brevets

(11)

Publication number:

**0 344 129**  
**A2**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 89830218.7

(51) Int. Cl.4: C 09 D 3/58

(22) Date of filing: 17.05.89

(30) Priority: 18.05.88 IT 4797788

(43) Date of publication of application:  
29.11.89 Bulletin 89/48(84) Designated Contracting States:  
BE DE ES FR GB SE(71) Applicant: CENTRO SVILUPPO MATERIALI S.p.A.  
P.O. Box 10747 Via di Castel Romano 100-102  
I-00129 Roma (IT)(72) Inventor: Colaiacovo, Ferdinando  
Via L. Greppi, 77  
Roma (IT)Derchi, Domenico  
Via Ovidio, 84  
Pomezia (Roma) (IT)Memmi, Massimo  
Via Cutigliano, 9  
Roma (IT)(74) Representative: Mariani, Giulio  
c/o Centro Sviluppo Materiali SpA P.O. BOX 10747  
I-00100 Roma Eur (IT)

(54) Organic coating for metals.

(57) The present invention provides a thin continuous organic coating on metals, particularly on continuous metal bodies, so that the product obtained is weldable and resistant to corrosion as well as to the effect of strongly acid and strongly alkaline baths, while being punchable and paintable. The coating according to the invention comprises organic resins characterized by ultimate elongation higher than 100%, electrical insulation resistance less than 2000 Ohm/cm<sup>2</sup>, able to produce a continuous coating on the metal substrate with micro-roughnesses (Ra) of about 3 µm - being Ra the average roughness - and capable of withstanding for thirty minutes liquids with pH between 2 and 12,5.

EP 0 344 129 A2



## Description

## Organic coating for metals

Present invention refers to an organic coating for metals such as Fe, Al and Cu, for instance, particularly continuous metal bodies like wires, strips or sheets, particularly of steel.

5 Such metal bodies are usually subjected to protective surface treatment.

In particular, steel sheet used in the automotive industry to produce car bodies must possess very high resistance to cosmetic and perforating corrosion, so it may be subjected to zinc-based surface treatments, after which it is painted.

10 In the case of such coatings, the Zn, which is sacrificial vis-à-vis Fe, oxidizes in the place of the latter. However, as the products of Zn oxidation have a high surface area, they produce blisters that adversely affect the appearance of the covering paintwork.

Moreover, during mechanical deformation and forming, electrogalvanized sheets tend to produce a large quantity of debris (powdering). Consequently, the surface of the sheet becomes marked and pitted and the coating is lost, so the amount of protection is decreased.

15 In order to improve corrosion resistance, therefore, organic coatings have been developed that can be applied directly to the bare sheet or to sheet that has been coated as indicated above. It has been found that the thickness of the organic coatings is a critical parameter, because although a thick coating increases corrosion resistance, it also reduces sheet weldability.

20 When applied in very thin layers (e.g. 2  $\mu\text{m}$  or less), organic coatings obtained with conventional resins have been considered unsatisfactory from the corrosion point of view (see pages 81 to 90 of SAE December 1986). The same article describes the development of thick organic coatings containing metal fillers which are added to obtain a good compromise between corrosion resistance and weldability when applied to metals. However, these fillers further intensify the quantity of powder produced during forming, hence aggravating the problems of sheet pitting. Furthermore, the fillers tend to settle out when the resin is being applied, causing serious applications problems.

25 An improvement in the field of organic coatings has been made with the introduction of silicate-modified resins as described on pages 49 to 54 of Nippon Kokan Technical Report Overseas No 34 (1982). But although these resins are applied in very thin layers, even in the order of 1  $\mu\text{m}$ , and are satisfactory from the weldability aspect, they are unsatisfactory where corrosion is concerned, especially following the alkaline degreasing to which the sheet is subjected after car-body assembly.

This unsatisfactory behaviour probably stems from poor adhesion of the organic coating to the metal, very likely because of coating deterioration in an alkaline medium.

Furthermore, because of the high temperature required for curing the resins employed, there is a decline in the mechanical properties of the metal substrate.

35 Quite evidently, therefore, an organic coating is needed that has better characteristics than those previously known.

A continuous organic coating thus been developed, as per this invention, for application to metals, especially continuous metal bodies, the coating being thin and such that the ensuing coated product is weldable, resistant to corrosion and to the effects of strongly acid and strongly alkaline baths, as well as being punchable and paintable.

40 The coating which forms the object of this invention includes organic resins characterized by ultimate elongation greater than 10%, electrical insulation resistance less than 2000  $\text{Ohm}/\text{cm}^2$ , ability to produce a continuous coating on the metal substrate, around thirty minutes resistance to liquids with a pH in the 2 to 12.5 range, and capability of coating micro-roughnesses (Ra) of about 3  $\mu\text{m}$ , where Ra is the average roughness parameter.

Hot or cold cross-linking or non cross-linking resins which can be applied as-is or dissolved in solvent or in a dispersion so as to produce continuous coatings with a thickness of 2  $\mu\text{m}$  or less and preferably between 0.5 and 1  $\mu\text{m}$  can be advantageously used for this purpose.

50 If the selected resin is of the hot cross-linking type, the resin should preferably cure at temperatures no higher than 200°C. Resins with a curing rate not exceeding two minutes are preferred.

The resins as per this invention can be applied for instance by dispersing them in an aqueous vehicle or by dissolving them in suitable solvents such as ketones, ethers, alcohols and in known aliphatic and aromatic compounds in general.

55 The resins can be applied on the metal substrate using known techniques such as, for instance, electrophoresis. However, the following known methods are particularly advantageous for obtaining uniform coatings having a constant thickness of between 0.5 and 2.0  $\mu\text{m}$  on continuous sheet:

- dipping the sheet in the coating bath containing the resins and regulation of thickness by means of grooved or sanded squeeze rollers

- coating using applicator rollers of the coil-coating type with a system of two or more rollers

60 In the case of this particular procedure, tests have been made on rollers with different degrees of hardness using solutions or dispersions containing resins of various viscosities.

It has been found that the best results as regards thickness and continuity of the deposited resin layer are obtained with rubber applicator rollers of hardness between 35 and 60 Shore A, and with the resin solution or

dispersion at a viscosity between 2 and 100 cP at 25°C, preferably 2 to 20 cP.

Resin adhesion to the metal substrate can be improved by known treatments such as chromate passivation, mixed oxide conversion and phosphating or by treatments like that described in USP 4 547 268.

A particularly interesting method of embodiment of the invention involves the use of epoxy resins:  
- in organic solvents such as cellosolve, methyl ethyl ketone, isobutyl alcohol, and curable with amines, amine adducts, phenolic resins, isocyanates and polysulphides known to the experts working in the field  
- in aqueous dispersion, applicable also via electrophoresis and curable with blocked isocyanates or melamine catalyzers, also known.

Some formulations within the ambit of the present invention are indicated below:

#### Formulation 1

A) Solid epoxy resin (epoxy equivalent 500) in 2 to 20% solution by weight in a solvent consisting of:

2 parts by weight of methyl isobutyl ketone

4 parts by weight of xylene

1 part by weight of isobutyl alcohol.

B) Isolated polyamine adducts in 50% solution by weight (equivalent active H about 370) in solvent consisting of:

4 parts by weight of xylene

4 parts by weight of polyglycol monomethyl ether

1 part by weight of isobutyl alcohol. A-B mixing ratio of 100/75.

Hardening can occur by curing at room temperature where needed for particular production problems or preferably at a temperature of 180°C.

#### Formulation 2

A) Solid epoxy resin (epoxy equivalent 1500-2000) in 3 to 20% solution in solvent consisting of:

1 part by weight of diacetone alcohol or cellosolve

1 part by weight of toluene or cellosolve acetate

B) Phenolic resin, 70% by weight in butyl alcohol.

B is added to A in quantities equal to 60-70% of A. Hardening occurs in the presence of known basic accelerators equal to 0.1-0.5% by weight of the mix at temperatures between 160 and 200°C.

Coatings as per the invention, applied on metal substrates at thicknesses of less than 2 µm, are continuous and cause no welding problems. Furthermore the coated bodies give excellent results when subjected to mechanical working, such as bending, deep drawing and forming. These bodies also acquire greater corrosion resistance and compatibility with such organic materials as cataphoretic and noncataphoretic paints applied subsequently.

A further advantage of products coated as per the invention stems from the fact that their use results in a decrease in the consumption of phosphating reagents used in the automotive industry, since these come to be applied only on such metal parts as are not resin coated.

The use of protective and forming oils is also eliminated.

Then, too, companies engaged on the production of household electrical appliances or on coil coating can advantageously use products coated as per the invention, since they can thus eliminate from the manufacturing process surface conversion treatments prior to painting. Plants can therefore be simpler and there are also ecological advantages, since polluting baths do not have to be used.

To explain the invention in greater detail a number of examples are given, but these must in no way be construed as limiting the scope and purposes of the invention.

The tests were performed on 0.75 mm thick steel specimens, two-side galvanized with Zn thickness of about 8 µm and roughness Ra of 1.8 to 2.0 µm.

The organic coating was applied to these specimens whose surfaces were activated through mixed oxide surface conversion obtained by using Italbonder's commercial product, Bonderite.

The application was made by dipping the specimens in the solution described as Formulation 1, the thickness of the resins being controlled by two squeeze rollers.

The average thickness of resin on the specimens was 0.8 µm.

The results of the characterization tests on the specimens coated as per the invention were compared with the corresponding results for bare specimens without any organic coating.

#### I Resistance to degreasing alkaline and acid phosphating baths

Degreasing bath: Industrial type alkaline soap, 5% concentration in water, pH 12, T 60°C, immersion time 7 minutes.

Phosphating bath: Industrial type zinc phosphating, pH 2.2, T 55°C, immersion time 3 minutes.

The coated specimens remained unaltered after immersion in the baths. The percentage of area found to have been destroyed or peeled off after this operation was less than 1% according to microscopic assessment.

**II Corrosion resistance**

Test conditions as per ASTM B117 with evaluation of the increase in time to appearance of red rust compared with specimens without the organic coating.

- 5 The coated specimens exhibited an increase in corrosion resistance more than 300% compared with the bare specimens.

**III Cathophoretic paintability and paint adhesion to substrate**

- 10 It was found that, under the same operating conditions, the thicknesses of cathophoretic paints deposited on the bare and the coated specimens are identical.

Wet Adhesion and Cathodic Wet Adhesion, between cathophoretic paint and organic film is comparable or better than that between paint and the best phosphate treatment for zinc.

Percent area peeled off			
		WA	CWA
20	Bare specimen	A	70
	Coated specimen	A	1
25	Bare specimen	B	3
	Coated specimen	B	<1
30	A = industrial phosphating cycle with high-Zn phosphating bath		
35	B = industrial phosphating cycle with Zn/Ni/Mn phosphating bath		
40	WA= Wet Adhesion CWA=Cathodic Wet Adhesion		

**Wet Adhesion**

Conditions:

- 45 - Incised with 2x2 mm grid  
 - Immersion in distilled water at 40°C for one week  
 - Covering test area with adhesive tape strip, and removing the same  
 - Evaluation with automatic image analyzer (QTM) of percent area of paint removed by the tape strip.

**50 Cathodic Wet Adhesion**

Conditions:

- 55 - Incised with 2x2 mm grid  
 - Immersion in 0.5 N NaCl solution at room temperature for 24 h and contemporary imposition of 30  $\mu\text{A}/\text{cm}^2$  cathodic current  
 - Covering test area with adhesive tape and removing the same  
 - QTM evaluation of percentage of paint removed by tape strip.

**IV Wear resistance during forming**

- 60 This test is performed pulling a strip of material through a clamping device having either a flat clamp and a convex clamp (flat tools) or a concave clamp and a convex clamp (draw-bead tools). In the latter case the strip moves obviously in a curved path.

- 65 In our tests bare and coated strips of 15x350 mm and 30x350 mm (with flat tools) and of 15x350 mm (for draw-bead tools) were pulled for 200 mm through testing devices, with a speed of 500 mm/min.

Bare specimens were lubricated.  
It was observed that un-lubricated coated strips suffered much less surface damage than lubricated bare specimens; in fact detritus collected from tests of bare specimens was 400% more abundant than detritus collected from tests of coated specimens.

5

#### **V Weldability**

Spot weldability conditions for sheet with an organic film are broader and there is a shift towards lower currents.

After 3000 spot welds on a pair of two-side-clad, superimposed sheets, there was no evidence of variations in the shear strength of the weld.

10

#### **Weldability conditions**

- Electrode diameter 5.5 mm
- Clamping load 2.3 kN
- Hold time (HT) 30 cycles (50 Hz)

15

20

#### **Claims**

1. Organic layer having a thickness of 2 or less  $\mu\text{m}$ , coated on metals, particularly continuous elongated metal bodies, such that obtained coated product is weldable, resistant to corrosion as well as to strongly acid and strongly alkaline baths, while being punchable, deformable and paintable, said coating including organic resins having an ultimate elongation in excess of 10% selected among solid epoxy resins having epoxy equivalent comprised between 500 and 2000, said coating being obtained dissolving said resins in a solvent chosen between water, cellosolve, methyl ethyl ketone and isobutyl alcohol containing also a curing agent selected between amines, amine adducts, melamines, phenolic resins, isocyanates and polysulphides, and applying the solution thus obtained onto said metal bodies.

25

30

2. Organic coating as per Claim 1 in which the resins are selected from among those that cure at temperatures no higher than 200°C.

3. Organic coating as per Claim 1 in which the resins are selected from among those that cure in a time not exceeding 2 minutes.

4. Process for application of resins as per Claim 1 to 5, on continuous metal strips in which the application is performed as per known processes such as coil coating, characterized by the fact that the applicator rollers are rubber of hardness between 5 and 60 Shore A, while the viscosity of the liquid medium containing the resin is between 2 and 100 cP at 25°C.

35

5. Process as per Claim 6 in which the viscosity of the medium is between 2 and 20 cP at 25°C. 6. Continuous metal bodies clad with organic coating as per Claim 1 to 5.

40

45

50

55

60

65